

Anomaly in Spin Excitation Spectrum of Double-Exchange Systems with Randomness

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Spin excitation spectrum of the double-exchange model is studied in the presence of randomness. Spin wave approximation in the ground state shows that the randomness significantly modifies the spectrum from the cosine-like one in the pure system to that with anomalies such as broadening, anti-crossing and gap opening. The origin of anomalies is speculated to be modulation of effective ferromagnetic coupling by the Friedel oscillation. These anomalies qualitatively reproduce the spin excitation spectrum in colossal magnetoresistance manganites whose Curie temperatures are relatively low. Our results suggest that randomness control is an important notion to understand effects of the A-site substitution which has previously been understood as the bandwidth control.

KEYWORDS: colossal magnetoresistance manganites, double-exchange model, randomness, spin dynamics, A-site substitution, bandwidth control

One of the most important issues of colossal magnetoresistance (CMR) manganites AMnO_3 is to understand effects of the A-site substitution.¹⁾ Generally, the A-site substitution has two different aspects. One is the carrier doping which is the substitution by A ions with different valences. The other is the ionic radius modification which is the A-site substitution with ions having the same valence but different ionic radius. In the latter, the averaged radius of A ions $\langle r_A \rangle$ affects length and angle of Mn-O-Mn bonds. This leads to a change of effective transfer energies between Mn sites. Therefore, it is widely accepted that the ionic radius modification gives a bandwidth control. Owing to a wide potential of these A-site substitutions, manganese oxides exhibit rich physics including the CMR phenomena.

Among various compounds AMnO_3 , recent developments in both experiments and theories have been revealed that $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) at $x \simeq 1/3$ is a canonical double-exchange (DE) systems.^{2,3)} The DE model⁴⁾ can explain magnetic and transport properties in this compound quantitatively. For instance, the experimental values of Curie temperature T_C agree well with the theoretical estimate.³⁾ Thus, the LSMO compound provides a well-established starting point to examine effects of the A-site substitutions.

Starting from LSMO as a reference, we focus on the ionic radius control by the A-site substitutions. This causes a systematic change in transport and magnetic properties. For instance, the value of T_C decreases systematically for compounds with smaller $\langle r_A \rangle$ and hence with ‘narrower-bandwidth’ such as $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (LCMO). Hereafter, we call these A-site substituted compounds ‘low- T_C manganites’ whereas we call the compounds such as LSMO, which show relatively high T_C , ‘high- T_C manganites’. An empirical relation between T_C and $\langle r_A \rangle$ has been proposed experimentally.⁵⁾

The systematic change has been considered to be primarily due to the bandwidth change by the A-site substitution.

However, the picture of the bandwidth control has been doubted by some experimental results. One is a quantitative comparison between T_C and the bandwidth estimated from $\langle r_A \rangle$. The change of T_C is much larger than that of the bandwidth. For instance, from LSMO to LCMO, T_C decreases about 30% while the estimated bandwidth decreases less than 2%.⁶⁾ This large decrease of T_C cannot be explained by the bandwidth control in the DE theory in which T_C should scale to the bandwidth. An extra degree of freedom as a hidden parameter seems to be necessary to explain such a change.

In this Letter, we examine a role of the randomness in the A-site substitution. In general, oxides are known to be far from perfect crystals. Moreover, in manganites, randomness is inevitably introduced by the A-site substitution since the compounds are solid solutions of different A ions. Random distribution of A ions induces a charge and structural disorder in the system, which introduces randomness in the electronic Hamiltonian.

Importance of the randomness effects has been discussed both experimentally and theoretically. One is that T_C is much affected not only by the averaged radius of A ions but also by the standard deviation of the ionic radii. A linear decrease of T_C as a function of the standard deviation has been reported.⁷⁾ Another experimental fact is a correlation between the residual resistivity and T_C . The A-site substitution from high- T_C to low- T_C manganites causes a systematic increase of the residual resistivity even in single crystals.^{8,9)} These results clearly indicate that it is necessary to take account of effects of the randomness in the A-site substitution. Recently, effects of the randomness have been discussed in the DE model.^{10,11,12,13)} A significant decrease of T_C

by the randomness has been predicted.^{10, 11, 14, 15, 16)}

Let us now consider another important result of the ionic radius modification which is the systematic change in the spin excitation spectrum. High- T_C manganites show a cosine-like spin-wave dispersion¹⁷⁾ which is well described by the DE theory quantitatively.¹⁸⁾ On the other hand, in low- T_C manganites, the spin excitation deviates from this behavior considerably, and shows some anomalies such as softening, broadening, anti-crossing and gap-opening.^{19, 20, 21, 22)} The DE theory also fails to explain these anomalies in the spin dynamics.

In this Letter, we study effects of the randomness on the spin dynamics in the DE model. The spin excitation is calculated in the ground state by the spin wave approximation. We find clear deviation from the cosine-like spin-wave dispersion in the pure DE model and some anomalies in the spin excitation spectrum. Through comparisons with the experimental results in low- T_C manganites, our results strongly suggest that the randomness gives an important effect of the A-site substitution.

As a model for the A-site substituted manganites, we consider the DE model with randomness. The Hamiltonian is written by

$$\mathcal{H} = -t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) - \frac{J_H}{S} \sum_i \vec{\sigma}_i \cdot \vec{S}_i + \sum_{i\sigma} \varepsilon_i c_{i\sigma}^\dagger c_{i\sigma}, \quad (1)$$

where the first two terms denote the DE Hamiltonian⁴⁾ which consists of the nearest-neighbor hopping and the Hund's-rule coupling between itinerant electrons and localized spins with a magnitude S . These two terms quantitatively describe physical properties in high- T_C manganites including the spin excitation.^{2, 3, 18)} The last term denotes the on-site randomness. In this work, for simplicity, we incorporate the randomness by the A-site substitution as the on-site random potential although it may cause various other effects, for instance, a randomness in transfer integrals. Here we consider the binary-alloy type randomness, that is, ε_i takes $\pm W_{\text{imp}}/2$ in equal probability in each site. We confirm that the results are independent of the type of randomness qualitatively. Although it is difficult to determine the actual magnitude of the randomness in manganites, the value of W_{imp} is roughly estimated to be the same order of magnitude as the bandwidth in low- T_C compounds.^{8, 23)} As an energy unit, we use the half bandwidth at the ground state for $W_{\text{imp}} = J_H = 0$, i.e., $W = 6t = 1$ in three dimensions.

We study the spin excitation of the model (1) using the spin wave approximation. We consider a perfectly spin-polarized ferromagnetic ground state $\vec{S}_i = (0, 0, S)$, and calculate the one-magnon excitation spectrum within the lowest order of $1/S$ expansion. In the absence of impurities, the formulation is given in Ref. 18.

Here we extend the method to the case with randomness. For a given configuration of the quenched randomness $\{\varepsilon\}$ on a finite size cluster, we explicitly diagonalize the Hamiltonian matrix at the ground state. We have

$$\mathcal{H} \tilde{\varphi}_{n\sigma}(i) = (\tilde{E}_n - \sigma J_H) \tilde{\varphi}_{n\sigma}(i), \quad (2)$$

where $\tilde{\varphi}_{n\sigma}$ is the n -th wavefunction for the spin σ elec-

tron. Since wavefunctions are given in real space, it is straightforward to formulate Green's functions of electrons and spin wave using the real-space representation.

Electron Green's function is given by

$$\tilde{G}_{ij, \sigma}(\omega) = \sum_n \frac{\tilde{\varphi}_{n\sigma}(i) \tilde{\varphi}_{n\sigma}^*(j)}{\omega - (\tilde{E}_n - \sigma J_H - \mu) + i\eta \text{sgn} \omega}. \quad (3)$$

Following Ref. 18, spin wave self-energy is calculated from electron's spin polarization function depicted in Fig. 1. In the limit of $J_H/t \rightarrow \infty$, which is realistic in manganites, we obtain

$$\tilde{\Pi}_{ij}(\omega) = \frac{1}{2SN} \sum_{mn} f_{n\uparrow} \tilde{\varphi}_{n\uparrow}(i) \tilde{\varphi}_{n\uparrow}(j)^* \tilde{\varphi}_{m\downarrow}(j) \tilde{\varphi}_{m\downarrow}(i)^* \times (\tilde{E}_m - \tilde{E}_n - \omega), \quad (4)$$

where N is the number of lattice sites and $f_{n\uparrow}$ is the fermi distribution function for up-spin states. Spin wave Green's function is given by $\tilde{D}_{ij}(\omega) = (\omega - \tilde{\Pi}_{ij}(\omega) + i\eta)^{-1}$. Spin wave excitations are obtained from the poles of the Green's function. Since $\tilde{\Pi}_{ij} \propto 1/S$, positions of poles are at $\omega \sim O(1/S)$. Then, as discussed in Ref. 18, spin wave excitations within the lowest order of $1/S$ expansion can be determined from the static part of the self-energy $\tilde{\Pi}_{ij}(\omega = 0)$.

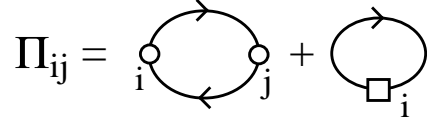


Fig. 1. Spin wave self-energy in the lowest order of the $1/S$ expansion. See Ref. 18 for details.

The spectral function for spin wave is defined by

$$\tilde{A}(\mathbf{q}, \omega) = -\frac{1}{N} \sum_{ij} \frac{1}{\pi} \text{Im} \tilde{D}_{ij}(\omega) \exp[i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)]. \quad (5)$$

Using the eigenvalues $\tilde{\omega}_l$ and eigenvectors $\tilde{\psi}_l(j)$ of $\tilde{\Pi}_{ij}$,

$$\sum_j \tilde{\Pi}_{ij}(\omega = 0) \cdot \tilde{\psi}_l(j) = \tilde{\omega}_l \tilde{\psi}_l(i), \quad (6)$$

the matrix inversion of $(\omega - \tilde{\Pi}_{ij})$ is obtained. We have

$$\tilde{A}(\mathbf{q}, \omega) = \sum_l \tilde{A}_l(\mathbf{q}) \delta(\omega - \tilde{\omega}_l), \quad (7)$$

$$\tilde{A}_l(\mathbf{q}) = \frac{1}{N} \left| \sum_j \tilde{\psi}_l(j) \exp(i\mathbf{q} \cdot \mathbf{r}_j) \right|^2. \quad (8)$$

Finally, we average $\tilde{A}(\mathbf{q}, \omega)$ for random configurations of the potential $\{\varepsilon\}$ to obtain the spectral function $A(\mathbf{q}, \omega)$.

Figure 2 shows the spectral function for spin excitations at $x = 0.3$ in three dimensions. Here, x is the hole density in model (1). System size N is $16 \times 16 \times 16$ with the periodic boundary conditions and the random average is taken for 24 different configurations of the random potential for each value of W_{imp} . For small values of W_{imp} , the spectrum is similar to the cosine-like dispersion for $W_{\text{imp}} = 0$ (gray curve) although it shows some

broadening. However, when the value of W_{imp} becomes moderate, some anomalies appear conspicuously in the spectrum. Apart from the large broadening, a remarkable feature is a branching which is clearly seen, for instance, along the Γ -M and Γ -R lines for $W_{\text{imp}}/W = 0.5$. Near the zone boundary, extra branches with considerable weight appear well below the cosine-like branch. If one follows only the extra lower branch, the spin excitation spectrum appears to show a significant softening.

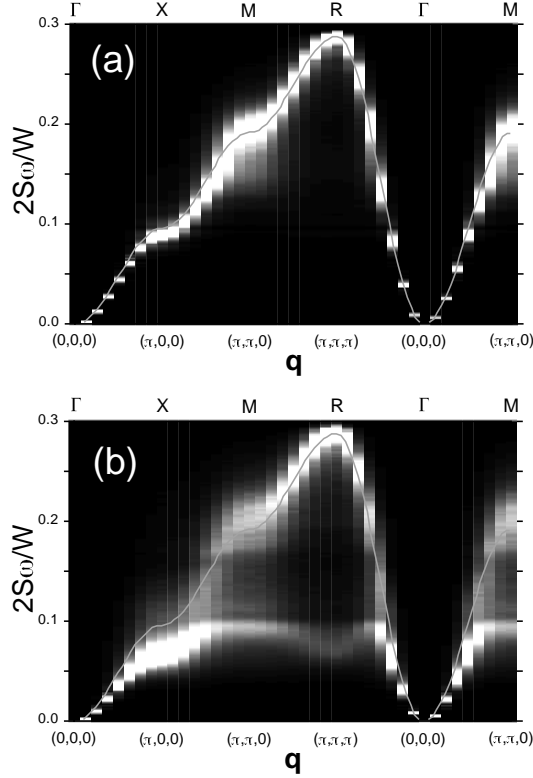


Fig. 2. Spin excitation spectra at $x = 0.3$ in three dimensions for (a) $W_{\text{imp}}/W = 0.2$ and (b) $W_{\text{imp}}/W = 0.5$. The intensity is shown by gray scale along the vertical axis. The discreteness along the horizontal axis comes from the fact that the calculations are performed on finite-size clusters. The gray curves are the spin wave dispersion in the pure case.

In order to consider the origin of the anomalies, we perform detailed calculations in one dimension. We take $N = 256$ and the random average for 500 configurations. Figure 3 shows the results for different values of x at $W_{\text{imp}}/W = 0.5$ ($W = 2t$ in one dimension). The precise calculations in one dimension reveal the detailed structure of the anomalies; an anti-crossing structure with a gap opening, shadow bands and a significant broadening. These remarkable features become conspicuous for the values of x far from the quarter filling $x = 0.5$.

An important point in Fig. 3 is that the anomalies appear near the Fermi wave number k_F which is given by $\pi(1-x)$ in one dimension. This indicates that the anomalies come from a singularity of $2k_F$ momentum transfer between $q \simeq k_F$ and $q \simeq -k_F$. There are also small anomalies at $q \simeq \pi - k_F$ and $-\pi + k_F$. We note that these anomalies can be seen even in the case with a single impurity. Namely, positions of anomalies in q -space scale with k_F , while the intensities of the anomalous parts de-

pend on impurity strength. From these observations, it is clear that the origin of the anomalies is the fermionic responses of the itinerant electrons to impurities.

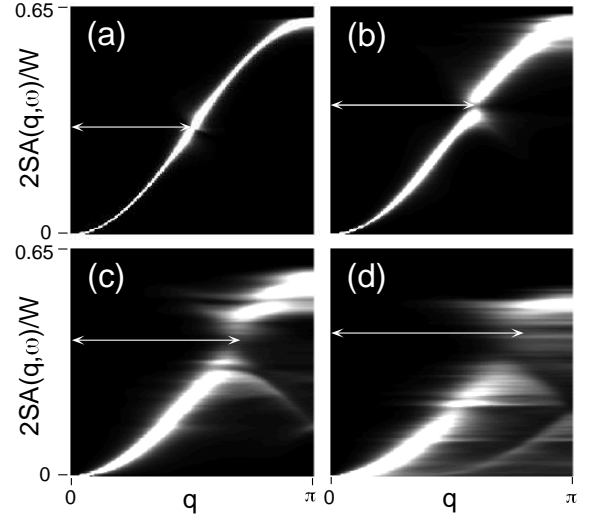


Fig. 3. Spin excitation spectra in one dimension for (a) $x = 0.5$, (b) $x = 0.4$, (c) $x = 0.3$ and (d) $x = 0.2$. The arrow in each figure indicates the magnitude of k_F .

We speculate that randomness induces modulation of effective exchange coupling due to the Friedel oscillation. The random potential causes the $2k_F$ singularity in the charge channel, which appears in the effective ferromagnetic coupling through the magnon-electron interaction. Scattering of magnons by the oscillating components of the exchange couplings creates the anti-crossing structure. The Friedel oscillation occurs universally in itinerant electron systems with randomness although its effect might be weaker in higher dimensions. Thus, the anomalies in three-dimensional systems in Fig. 2 may be an analog of the anti-crossing due to the Friedel oscillation.

We discuss our findings in comparison with experimental results. Our results reproduce the anomalies of spin excitations reported in low- T_C compounds qualitatively: (i) The spectrum shows a significant broadening near the zone boundary.^{19,20,21,22} (ii) The softening near the zone boundary^{19,21,22} can be interpreted as a consequence of the branching or the anti-crossing in our results. The lower-energy branch has a substantial weight and is easily identified in neutron scattering experiments, while the higher-energy one may be difficult to identify due to a deficiency of energy resolution in experiments. (iii) The anti-crossing or the gap opening^{20,22} have been reproduced. Thus, the randomness is reasonably considered as a hidden parameter to give a qualitative description for the anomalous spin dynamics in low- T_C manganites.

Several other scenarios have also been proposed to explain the spin excitation spectrum in low- T_C manganites. As an origin of the softening, some additional elements to the DE mechanism have been examined such as magnon-orbital²⁴ and magnon-phonon couplings.²⁵ Magnetic origin has also been proposed.²⁶ For the origin of the broadening, magnon-phonon²⁴ or magnon-

electron couplings²⁷⁾ have been discussed. These arguments attribute the origin of the spectrum change by the A-site substitution to the modification of the bandwidth through some additional couplings to the spin degrees of freedom. As discussed previously, however, the actual changes of the bandwidth in these compounds are small. Therefore, it seems difficult for these scenarios to explain the large changes of the spin excitations in a quantitative manner. Moreover, neither the anti-crossing nor the gap opening has been reproduced by them.

Our results give a comprehensive scenario to understand the systematic changes of spin excitations in the A-site substituted manganites, since the change of the randomness are expected to be large, as previously discussed in reproducing the systematic decrease of T_C . We suggest that the randomness gives important effects on various thermodynamic properties of A-site substituted manganites.

We now propose some experimental tests for our scenario. One is the sample dependence. Our scenario predicts a correlation between the sample quality and the anomalies in the spin wave spectrum. Therefore, even in compounds with the same chemical formula, the extent of the anomalies would depend on the purity of samples which is measured independently, for instance, by the residual resistivity. The second test is to investigate the location of the anomalies in the whole Brillouin zone, and to make a comparison with information of the Fermi surface, which is obtained by independent experiments, for instance, by the angle-resolved photoemission. The anomalies appear at the Fermi wave number in our scenario. Doping dependence is also crucial in this test. The third is to observe the high energy excitation near the band top $\mathbf{q} \simeq (\pi, \pi, \pi)$. In our results, there remains an excitation with substantial weight and relatively sharp peak-width near the band top even under strong randomness. This may be observed by the pulse-neutron scattering. All these experimental tests are feasible and may help to discuss the origin of the anomalies in the spin excitation as well as the role of the A-site substitution in CMR manganites.

Finally, we comment on higher-order corrections in the $1/S$ expansion. The aim of this Letter is to study the systematic changes of the spectrum by the A-site substitution of manganites. In this case, the parameter $1/S$ should be kept fixed, and the $1/S$ expansion does not contribute to the spectrum changes. Furthermore, it has been shown that the contribution of the higher order terms are very small at $x \simeq 1/3$ where we are interested in, at least in the pure case.^{28, 29)} Therefore, we conclude that the lowest order terms in the $1/S$ expansion is sufficient to discuss the randomness effects as a first step, although quantitative estimates of the $1/S$ corrections in the presence of randomness are left for further studies.

To summarize, we have investigated effects of randomness on the spin excitation spectrum in the double-exchange model. The spin dynamics in the ground state is calculated by the spin wave approximation in the lowest order of the $1/S$ expansion. Randomness induces some anomalies in the spectrum near the Fermi wave number such as the broadening, the anti-crossing and

the gap opening. We speculate that the origin of the anomalies is modulation of effective exchange coupling by the Friedel oscillation. The anomalous spin dynamics in CMR manganites is reproduced qualitatively. Since the anomalies in experiments become conspicuous in A-site substituted compounds which have low Curie temperature, our results suggest that the randomness is an important element in the A-site substitution which has previously been understood as the bandwidth control. We have discussed our results in comparison with other theories and proposed several crucial experimental tests.

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